Volatile aromatic hydrocarbon concentrations in heavy fuel oil and the atmosphere collected from seashores affected by an oil spill

VOLATILE AROMATIC HYDROCARBON CONCENTRATIONS IN HEAVY FUEL OIL AND THE ATMOSPHERE COLLECTED FROM SEASHORES AFFECTED BY AN OIL SPILL

Tsuyoshi MURAHASHI[1,2], Ryoichi KIZU[2] and Kazuichi HAYAKAWA[2]

[1] Kyoto Pharmaceutical University, 5 Misasagi-Nakauchi-cho, Yamashina-ku, 607-8414 Kyoto, JAPAN; e-mail: tmu@mb.kyoto-phu.ac.jp
[2] Faculty of Pharmaceutical Sciences, Kanazawa University, 13–1 Takara-machi, 920-0934 Kanazawa, JAPAN

ABSTRACT

Volatile aromatic hydrocarbons (benzene, toluene and xylenes) were determined in heavy fuel oil and in the atmosphere at seashores affected by the Nakhodka tanker oil spill. The oil from the Nakhodka tanker contained 8.8 μg g^{-1} of benzene, 120 μg g^{-1} of toluene and 131 μg g^{-1} of xylenes. Benzene, toluene and xylene concentrations in the atmosphere at sites where spilled oil was collected ranged from ND (not detected)–1.65, ND–11.70 and ND–50.16 μg m^{-3}, respectively. Their concentrations were lower on the beach and higher when collected by a volunteer who carried an air sampler. However, these concentrations were more than two orders of magnitude lower than threshold limit values. To determine vaporization of aromatic hydrocarbons from the oil, time courses of aromatic hydrocarbon concentrations in the gas phase were determined in the laboratory. High concentrations of toluene (28 μg m^{-3}), xylenes (98 μg m^{-3}) and naphthalene (84 μg m^{-3}) were observed after 72 h. These results suggest that volunteers who collect spilled oil soon after a spill might be exposed to high concentrations of toluene, xylene and naphthalene.

INTRODUCTION

A Russian tanker "the Nakhodka" sank off the coast of Shimane Prefecture on January 2, 1997. A large amount of heavy fuel oil (6,200 kL) was spilled from the tanker, and the spilled oil reached Katano Beach in Kaga City, Ishikawa Prefecture on January 8. The oil then reached beaches in Kanazawa, Wajima and Suzu City, Ishikawa Prefecture. Volunteers, local residents and a self-defense force collected the spilled oil. However, many volunteers suffered from headaches, dizziness and vomiting.

C-heavy fuel oil contains small amounts of volatile aromatic hydrocarbons such as benzene, toluene and xylenes. Exposure to these aromatic hydrocarbons can cause effects such as headaches, dizziness and vomiting. We therefore measured volatile aromatic hydrocarbon concentrations in the oil from the Nakhodka tanker, and in the atmosphere at sites where spilled oil was collected from the seashores of the Nagahashi and Kurasaki Beaches.

METHODS

Preparation of the oil from the Nakhodka tanker

C-heavy fuel from the stem head of the Nakhodka tanker was diluted with CS_2. Benzene, toluene, xylenes and naphthalene were determined by using a gas chromatography/mass spectrometry (GC/MS) system. (Hayakawa *et al.*, 1997)

Sampling and pretreatment of air at seashore

Air was sampled by a Sibata MP-15CF personal air sampler connected to a Sibata charcoal tube (Figure 1). Sampling was carried out from January 30 to February 1, 1997. Sampling points at the Nagahashi and Kurasaki Beaches in Suzu City, Ishikawa Prefecture are shown in Figure 2. Sampling point no.1 was on Nagahashi Beach, no.2 was in the aid station, and no.3 was beside a pool of collected oil. Sampling points nos. 1–3 were stationary. Sampling point no.4 was on Kurasaki Beach, 1.4 km west of Nagahashi Beach. At this sampling point, a volunteer carried a personal air sampler. Aromatic hydrocarbons adsorbed on charcoal were extracted with CS_2 for 2 h. An aliquot of the solution was injected into a GC/MS system.

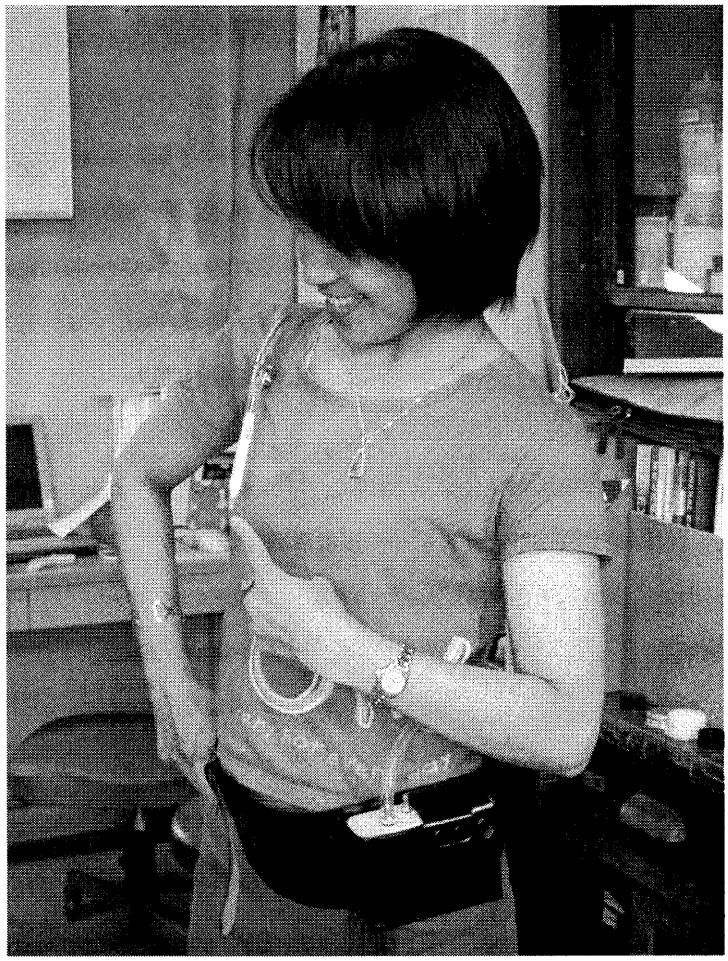

Figure 1 Photograph of a personal air sampler.

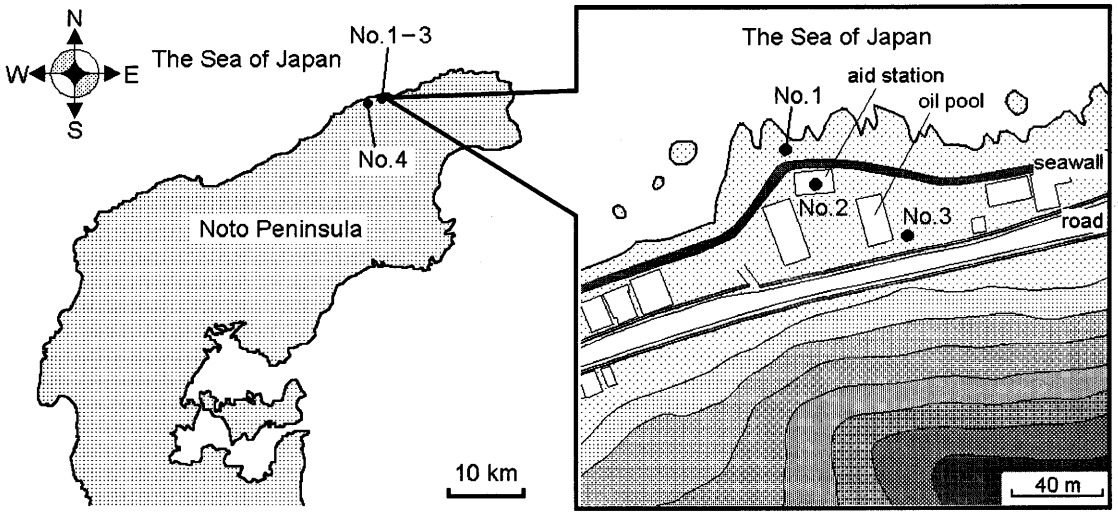

Figure 2 Air sampling locations.

Laboratory experiment

The equipment used in the laboratory experiment is shown in Figure 3. The oil from the Nakhodka tanker (10 g) was floated on seawater (500 ml) in a 1,000-ml glass flask. Seawater was stirred at a temperature of 10°C. Volatile aromatic hydrocarbons in air were adsorbed onto charcoal by passing air through a charcoal tube at a flow rate of 1,000 mL min^{-1} for 5–15 min. Aromatic hydrocarbons adsorbed on charcoal were extracted with CS_2 for 2 h. An aliquot of the solution was injected into a GC/MS system.

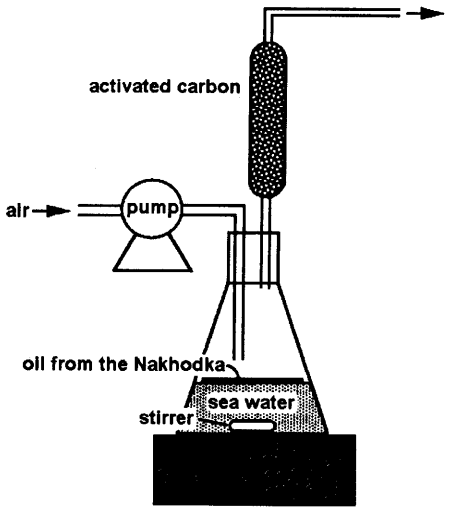

Figure 3 Equipment used in the laboratory experiment.

GC/MS

GC/MS determination was performed by using a Shimadzu GC-14A gas chromatograph coupled to a Shimadzu GCMS-QP2000 mass spectrometer. A Hewlett-Packard Ulbon HR-1 capillary column (50 m × 0.25 mm i.d.) was used for the separation of volatile aromatic hydrocarbons. The oven was temperature programmed as follows: 30°C for 3 min, increased at 10°C min^{-1} to 300°C, and held at 300°C for 10 min. MS detection was performed in selected ion monitoring (SIM) mode. Monitoring ions (*m/z*) were 78 for benzene, 92 for toluene and xylenes, 128 for naphthalene and 166 for fluorene.

RESULTS AND DISCUSSION

A large number of volunteers collecting oil from the seashore in the vicinity of the Nakhodka tanker oil spill were observed to develop headaches, dizziness and vomiting. Symptoms of benzene overexposure by inhalation are dizziness, headache, vomiting, visual disturbances, staggering gait, hilarity, fatigue, CNS depression, loss of consciousness and respiratory arrest (Merck, 1999). Although symptoms of toluene and xylenes overexposure are almost identical, toxicities of toluene and xylenes are lower than that of benzene (Merck, 1999). Thus, we first determined volatile aromatic hydrocarbon concentrations in the oil from the stem head of the Nakhodka tanker.

Table 1 lists volatile aromatic hydrocarbon concentrations in the oil from the Nakhodka tanker. The oil contained 8.8 μg g^{-1} of benzene, 120 μg g^{-1} of toluene and 131 μg g^{-1} of xylenes. Although toxicities of toluene and xylenes are lower than that of benzene, concentrations of toluene and xylenes were found to be much higher than that of benzene. We also detected two polycyclic aromatic hydrocarbons, naphthalene and fluorene. Naphthalene (a two-ring polycyclic aromatic hydrocarbon), and fluorene (a three-ring polycyclic aromatic hydrocarbon), were detected in the oil at concentrations of 408 and 126 μg g^{-1}, respectively. Concentrations of naphthalene and fluorene were found to be higher than those of toluene and xylenes.

Table 1 Volatile aromatic hydrocarbon concentrations in heavy fuel oil from the Nakhodka tanker.

Chemical	Boiling point (°C)	Concentration (μg g^{-1})
Benzene	80.1	8.8
Toluene	110.6	120
m- and *p*-Xylenes	139.3 (*m*-), 137–138 (*p*-)	43
o-Xylene	144	88
Naphthalene	218	408
Fluorene	295	126

We then measured benzene, toluene and xylenes in the air in areas where spilled oil was collected from seashores. We selected four sampling points. No.1 was a stationary sampling point on Nagahashi Beach. Many volunteers collected spilled oil at this sampling point. No.2 was a stationary sampling point in the aid station. Volunteers took a break and recovered at this sampling point. No.3 was also a stationary sampling point, near a pool of collected spilled oil. No.4 was a mobile sampling point on Kurasaki Beach. A volunteer carried a personal air sampler at this point. Sampling was carried out from January 30 to February 1, 1997.

Benzene, toluene and xylene concentrations in the atmosphere at sites where spilled oil was collected are listed in Table 2. Benzene, toluene and xylene concentrations ranged from ND (not detected) –1.23, ND–2.46 and ND–2.25 $\mu g\ m^{-3}$, respectively, at sampling point no.1 on the beach. At sampling point no.2, in the aid station, higher concentrations of benzene (1.04–1.65 $\mu g\ m^{-3}$), toluene (3.04–5.37 $\mu g\ m^{-3}$) and xylenes (7.74–19.99 $\mu g\ m^{-3}$) were observed, probably because sampling point no.2 was inside the room. Although sampling point no.3 was near the collected spilled oil, concentrations of benzene (0.77–1.64 $\mu g\ m^{-3}$), toluene (1.17–3.64 $\mu g\ m^{-3}$) and xylenes (1.33–1.67 $\mu g\ m^{-3}$) at sampling point no.3 were lower than those at no.2. At sampling point no.4, i.e. at the volunteer who collected spilled oil, benzene was not detected, but toluene (11.70 $\mu g\ m^{-3}$) and xylenes (50.16 $\mu g\ m^{-3}$) concentrations were much higher than those at sampling point no.2. These results suggest that volunteers who collected spilled oil might have been exposed to high concentrations of toluene and xylenes.

ACGIH (American Conference of Governmental Industrial Hygienists) has evaluated TLVs-TWA (threshold limit values – time weighted average) of benzene, toluene and xylenes as 0.5 ppm (1.6 mg m^{-3}), 50 ppm (180 mg m^{-3}) and 100 ppm (420 mg m^{-3}), respectively. Concentrations of benzene, toluene and xylenes observed in the air in the vicinity of the collection of spilled oil at seashores were found to be more than two orders of magnitude lower than the TLVs.

Table 2 Volatile aromatic hydrocarbon concentrations in the atmosphere at sites where spilled heavy fuel oil was collected.

Site	Date	Time	Weather	Atmospheric concentration (μg m^{-3})			
	(Y/M/D)	(h:m)		Benzene	Toluene	*p*+*m*-Xylene	*o*-Xylene
No.1	97/01/30	11:30–13:30	snow	0.97	1.72	0.30	0.09
No.1	97/01/30	13:40–15:40	snow	ND	ND	ND	ND
No.1	97/01/31	10:40–12:40	cloudy	0.98	1.69	1.69	0.56
No.1	97/01/31	12:45–14:45	cloudy	0.87	2.23	0.77	0.28
No.1	97/02/01	08:30–10:30	cloudy	1.32	2.46	0.86	ND
No.1	97/02/01	10:30–12:30	cloudy	0.97	2.20	0.62	0.21
No.2	97/01/30	11:45–13:45	snow	1.26	3.47	8.66	4.12
No.2	97/01/30	13:50–15:50	snow	1.04	3.04	6.18	2.86
No.2	97/01/31	10:45–12:45	cloudy	1.39	5.37	14.50	5.49
No.2	97/01/31	12:50–14:50	cloudy	1.65	5.27	12.95	5.67
No.2	97/02/01	08:45–10:45	cloudy	1.62	4.17	5.50	2.32
No.2	97/02/01	10:45–12:45	cloudy	1.22	3.17	5.38	2.36
No.3	97/01/31	10:50–12:50	cloudy	0.77	1.17	1.23	0.38
No.3	97/01/31	12:55–14:55	cloudy	0.93	1.55	1.05	0.28
No.3	97/02/01	08:40–10:40	cloudy	1.64	3.64	1.30	0.36
No.3	97/02/01	10:45–12:45	cloudy	1.25	2.51	1.05	0.62
No.4	97/01/30	10:45–12:45	snow	ND	11.70	33.84	16.32

ND, not detected.

To establish vaporization of aromatic hydrocarbons from the oil, time courses of aromatic hydrocarbon concentrations in the gas phase were measured. The oil floated on seawater, and the seawater was stirred. Results are listed in Table 3. Maximum concentrations of toluene and xylenes (28 μg m^{-3} for toluene, 98 μg m^{-3} for xylene) were observed at 72 h, and their concentrations decreased with increasing time. A high naphthalene concentration (84 μg m^{-3}) was observed at 72 h, and its concentration was higher than that of toluene. The above results suggest that volunteers who collected spilled oil soon after the spill might have been exposed not only to toluene and xylene, but also to naphthalene.

Table 3 Time courses of aromatic hydrocarbon concentrations ($\mu g\ m^{-3}$) in gas phase at 10°C

Time (h)	Benzene	Toluene	*p+m*-Xylene	*o*-Xylene	Naphthalene
72	NA	28	67	31	84
146	NA	15	34	13	5
197	NA	12	28	12	0
332	NA	8	22	9	0
575	NA	4	8	3	0

NA, not analyzed.

CONCLUSION

The heavy fuel oil from the Nakhodka tanker contained 8.8 $\mu g\ g^{-1}$ benzene, 120 $\mu g\ g^{-1}$ toluene, 131 $\mu g\ g^{-1}$ xylenes, 408 $\mu g\ g^{-1}$ naphthalene and 126 $\mu g\ g^{-1}$ fluorene. Concentrations of toluene, xylenes, naphthalene and fluorene were much higher than that of benzene.

Benzene, toluene and xylene concentrations in the atmosphere around the areas where spilled oil was collected were in the range of ND–1.65, ND–11.70 and ND–50.16 $\mu g\ m^{-3}$, respectively. Their concentrations were lower on the beach and higher at a sampler carried by a volunteer. However, these concentrations were more than two orders of magnitude lower than threshold limit values.

To determine vaporization of aromatic hydrocarbons from heavy fuel oil, time courses of aromatic hydrocarbon concentrations in the gas phase were determined. High concentrations of toluene (28 $\mu g\ m^{-3}$), xylenes (98 $\mu g\ m^{-3}$) and naphthalene (84 $\mu g\ m^{-3}$) were observed at 72 h. These results suggest that volunteers who collected spilled oil soon after the spill might have been exposed to high concentrations of toluene, xylene and naphthalene.

Acknowledgements

The authors thank Dr. Sumio Goto for lending personal samplers and volunteers for air sampling.

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